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## MECHANISM OF FORMATION OF REDOX POTENTIAL IN GLASS

A. B. Atkarskaya<sup>1</sup> and V. I. Kiyan<sup>1</sup>Translated from *Steklo i Keramika*, No. 1, pp. 12 – 14, January, 2002.

It is demonstrated that the redox potential (ROP) of glass is formed depending on the type of gases released in heating batch materials. The ROP of glass has a significant effect on the valence state of iron and copper and the oxygen coordination number of Cu(II) ions.

Light transmission in glass is mainly determined by the concentration of the colorant impurities from *d*- and *f*-elements that penetrate into a glass melt with the batch materials. The colorant capacity of each element is unique and is closely related to its valence-coordination state [1]. Thus, among the traditional glass impurities, CoO<sub>4</sub>, NiO<sub>4</sub>, Fe(II), Cr(III), and Cu(II)O<sub>6</sub> absorb more intensely in the visible range than CoO<sub>6</sub>, NiO<sub>6</sub>, Fe(III), Cr(IV), and Cu(II)O<sub>4</sub>, whereas Cu(I) has virtually no coloring effect on the glass melt.

The degree of oxidation of the variable-valence elements is influenced by the redox potential (ROP) of the glass melt, whose formation is determined by the ROP of the glass matrix and the batch and also by the temperature-time and redox conditions of glass melting [2, 3].

The effect of individual raw materials on the ROP of a batch for glass intended for construction and engineering is analyzed in [4]. The problem of estimating the ROP of optical glasses is not considered in detail in the technical literature.

The purpose of the present study is to consider the mechanism of the effect of the batch materials on the ROP of optical glasses. Copper and iron that are variable-valence elements were selected as indicators of the ROP of the glass melt [5]. A transformation of the spectral curves of absorption indexes and an increase or decrease in the intensity of the maximums make it possible to reliably estimate the variations in the level of acidity (alkalinity) of glass [5].

It is known that Cu(I) does not color the visible spectrum range, the Cu(II)O<sub>6</sub> complex (blue) is characterized by a band in the near IR range around 800 nm, Cu(II)O<sub>4</sub> (yellow) has a band in the violet range [6], and Cu(0) imparts a red color to glass (copper ruby).

Trivalent iron in glass has intense absorption near 380 nm, and bivalent iron has a blurred wide band with a maximum around 1000 nm [1].

The glass for experiments was melted from a traditional (a dry thoroughly averaged mixture of materials) or nontraditional batch. The latter was synthesized from silicon-containing sol-gel solutions by thermal coagulation and subsequent drying of gel [7]. The resulting powder was used for melting silicate glass. The phosphate glasses were obtained from true aqueous solutions containing all the necessary oxides [8].

The chemical materials used for batch preparations were oxides, hydroxides, acids, and salts of at least “analytical purity” grade. To perform the necessary measurements, 0.3% of iron was introduced via Fe<sub>2</sub>O<sub>3</sub>, or 0.1% copper was introduced via CuO into the batch of clear glasses.

The glass was melted in a laboratory electrical furnace in platinum, corundum, or quartz glass crucibles. In some cases the glass melt was subjected to 30 min swirling using oxygen, steam, or ammonium.

The spectral light transmission of glass was measured using a SF-26 spectrophotometer within a wavelength interval of 360 – 1100 nm. The absorption index  $a_\lambda$  of glass or the specific absorption index  $\chi_\lambda$  of the colorant impurity in glass was calculated from the formulas

$$a_\lambda = \frac{-\log \tau - D}{d},$$

$$\chi_\lambda = \frac{-\log \tau - D}{dW},$$

where  $\tau$  is the light transmission coefficient, %;  $D$  is the reflection correction;  $d$  is the sample thickness, cm;  $W$  is the weight content of the impurity, %.

All experiments were performed on three glass compositions: clear optical borosilicate glass K-8, tinted optical phosphate glass SZS-22, and photochromic glass FKHS-7. The indicators of variation in the acidity (basicity) of glasses were variable-valence elements: copper, which makes part of SZS-22 and FKHS-7 compositions, and iron, which was de-

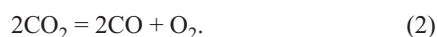
<sup>1</sup> K. I. Bondarev Avtosteklo Production Company, Konstantinovka, Ukraine.

liberately introduced into the batch of K-8 clear glass for estimating its ROP.

It is known that heating of a batch in charging leads to a decomposition of its material components and emission of gases. The nitrates in decomposition release oxygen, which is a strong oxidizer, and other gases at a high glass-melting temperature (1000 – 1500°C) can undergo thermal dissociation, react with each other, and form products that have a high oxidizing or reducing capacity. Thus, at a temperature around 500°C ammonia completely decomposes with the release of hydrogen, which is a strong reducing agent:

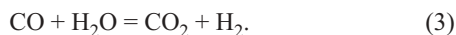


At 1000°C carbon dioxide (99.3% of it) dissociates according to the reaction



In this way an oxidizing gas ( $\text{O}_2$ ) and a reducing gas (CO) are formed.

Carbon monoxide at a temperature of 700°C or above reacts with water vapor:



One of the products of this reaction is hydrogen, which is a reducing agent.

Thus, it can be expected that the presence of ammonium salts, carbonates, hydroxides, and acids in a batch ought to increase the redox potential of the glass melt and raise the share of the low-valence forms of iron and copper, namely, Fe(II), Cu(I), and Cu(0) in the melt. It can be also assumed that insufficient oxidizing conditions in melting would influence the coordination environment of Cu(II) and modify its oxygen coordination number.

Since nitrates in their decomposition release oxygen, they should increase the redox potential of a glass.

For a quantitative estimation and an analysis of the effect of nitrates and carbonates on the ROP of a glass, the content of Fe(II) in the alkali-borosilicate glass K-8 was determined using a spectrophotometric method [9].

In the first stage the batch for K-8 glass was prepared from nitrates of alkaline and alkaline-earth metals, boric acid, and silicon dioxide. Iron (0.3%) was introduced into the batch via  $\text{Fe}_2\text{O}_3$ . In the second stage carbonates were used instead of nitrates.

Nitrates of alkaline metals when heated decompose, releasing oxygen, which increases the oxidizing capacity of the melt; accordingly, the share of Fe(II) in the glass is equal to 4.3%.

Carbonates decompose, forming  $\text{CO}_2$ , which at a high temperature is capable of dissociating according to reaction (2); the emerging CO according to reaction (3) reacts with water vapor, which is formed in heating boric acid. These

TABLE 1

Na <sub>2</sub> O content introduced into batch via		Photochromic properties*			Glass tint
NaNO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	μ <sub>0</sub> , %	μ <sub>5</sub> , %	μ <sub>5</sub> <sup>1</sup> , %	
1.00	0	17	22	19	Clear green
0.67	0.33	14	64	44	The same
0.50	0.50	13	62	44	"
0.33	0.67	14	68	49	"
0	1.00	Opaque glass			Liver

\* μ<sub>0</sub> is the initial light absorption of glass 2 mm thick; μ<sub>5</sub> is the light absorption of glass 5 min after UV activation on an IFS-2 standard plant; μ<sub>5</sub><sup>1</sup> is the light absorption of glass after 5 min of its spontaneous decolorization after UV activation.

two reactions in combination intensify the reducing potential of the glass, in which the content of Fe(II) grows to 7.8%.

The results of a gas chromatographic analysis of K-8 glass corroborate the existence of reaction (3), which is accompanied by emission of hydrogen in melting boron-bearing glass. The partial pressure at 1100°C is as follows (Pa): 9405 for H<sub>2</sub>O, 95 for (CO + CO<sub>2</sub>), 25 for N<sub>2</sub>, and 93 for H<sub>2</sub>. Note that K-8 glass was melted in a laboratory electric furnace from the traditional batch, and oxides of alkaline-earth metals were introduced in the batch via nitrates and carbonates, as is standard for the practice of optical glass production.

The presence of CO in gases extracted from glass corroborates the possibility of the reaction of thermal dissociation of carbon dioxide, which is released in the decomposition of carbonates, in the glass melt. The presence of hydrogen indicates a reaction of the water vapor formed in decomposition of boric acid with carbon monoxide according to reaction (3).

Consequently, the effect of materials on the ROP of a glass should be considered in the context of the nature of the gaseous products released in the decomposition of the batch materials and the reactions between these products. Nitrates releasing oxygen, when heated, increase the oxidizing potential of K-8 glass, whereas carbonates and boric acid decomposing with the formation of CO<sub>2</sub> and H<sub>2</sub>O decrease this potential. This is substantiated by the increase in the Fe(II) content from 4.3 to 7.8%.

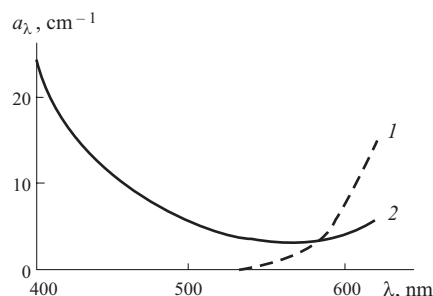
The photochromic glass FKHS-7 belongs to a sodium-borosilicate system complicated by small quantities of oxides of other elements; copper acts here as the light-sensitive component.

It is known that the photochromic properties of such glass are determined by the equilibrium



which is closely related to the ROP of the glass melt.

Table 1 shows the shares of NaNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> in a nontraditional batch of FKHS-7 glass and some properties of this glass.



**Fig. 1.** Copper absorption indexes in SZS-22 glass melted from a nontraditional batch based on nitrates (1) and ammonia salts (2).

It follows from the data in Table 1 that the increased content of sodium carbonate in the batch correlates with an increasing amount of the low-valence forms of copper up to the emergence of Cu(0) and points to a decreasing oxidizing potential of the glass. These data agree with the results of the variation of the ROP in K-8 glass.

Thus, the gases released in the decomposition of the materials affect the ROP of glass and indirectly affect the equilibrium of the valence forms of iron and copper.

It is known that the melting conditions do not have a perceptible effect on the coordination environment of nickel and cobalt, which depends only on the glass composition [1]. Accordingly, it can be expected that the capacity of bivalent copper for forming tetrahedra (yellow complex) or octahedra (blue complex) with oxygen is likely to be insensitive to a variation of the ROP of the glass depending on the type of materials. In order to prove or disprove this assumption, a batch of copper-tinted phosphate glass SZS-22 was prepared using nitrates or ammonium salts of the needed oxides.

Ammonium salts decompose in heating, releasing  $\text{NH}_3$ , which at a temperature over  $500^\circ\text{C}$  dissociates according to reaction (1) with the formation of a strong reducing agent, namely, hydrogen.

Figure 1 shows the copper absorption indexes in glass SZS-22 depending on the type of material used, which determines the ROP of the glass melt. The nitrates contribute to increasing the oxidizing potential and facilitate the formation of  $\text{Cu(II)O}_6$  with an absorption band around 800 nm. Ammonium salts, on the contrary, decrease the oxidizing (and increase the reducing) potential of the glass melt and facilitate the formation of tetrahedra  $[\text{Cu(II)O}_4]$  absorbing in the violet range of the spectrum.

Thus, the coordination state of the Cu(II) colorant ion largely depends on the ROP of the glass melt, and this coordination number grows from 4 to 6 as the oxidizing potential of the glass increases (the reducing potential decreases).

To verify the validity of the mechanism responsible for the effect of raw materials on the ROP of the glass melt, a copper-tinted melt of silicate glass K-8 produced from identical materials was subjected to swirling for 30 min at the clarification temperature using one of the gases below.

Gas	Specific index of copper absorption at a wavelength of 800 nm, $\text{cm}^{-1}$ per 1% copper
Oxygen . . . . .	15.2
Without swirling . . . . .	9.8
Water vapor. . . . .	7.5
Ammonia . . . . .	Liver-tinted opaque glass

Consequently, the oxidizing potential of the glass decreases (the reducing potential increases) in the following sequence:

$$\text{ROP of O}_2 > \text{ROP without swirling} > \text{ROP of H}_2\text{O} > \text{ROP of NH}_3.$$

This agrees with the described results and confirms the validity of the proposed mechanism of the effect of batch materials on the ROP of glass.

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